Cationic State Distributions over Chlorophyll Pairs in Photosystem I and II

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Abstract

Photosystem I (PSI) and II (PSII) possess chlorophyll pairs P_A/P_B and P_{D1}/P_{D2}, respectively. These chlorophylls are the primary electron donors in the light-induced electron transfer. After the electron transfer, the radical cation remains on these chlorophyll pairs, forming $[P_A/P_B]^{\bullet+}$ and $[P_{D1}/P_{D2}]^{\bullet+}$. The positive charge distributions over the two chlorophylls were reported to be different between PSI and PSII. To clarify the origin of the distributions, we calculated ratios of $P_A^{\bullet+}/P_B^{\bullet+}$ and $P_{D1}^{+}/P_{D2}^{\bullet+}$ with a quantum mechanical/molecular mechanical (QM/MM) approach and the redox potentials of monomeric chlorophylls P_A, P_B, P_{D1} and P_{D2} with an electrostatic continuum-model approach, using the crystal structures. Our calculation shows that in PSII the difference in the electrostatic protein environments between D1 and D2 was significant in determining the $P_{D1}^{+}/P_{D2}^{\bullet+}$ ratio, whereas geometric differences between P_A and P_B (P_A as the $C13^2$ epimer of chlorophyll *a* and the H-bond pattern) played a role in determining the $P_A^{\bullet+}/P_B^{\bullet+}$ ratio in PSI.

Purpose

To clarify the origin of determining the positive charge distributions over the chlorophyll monomers of the $[P_A/P_B]$ and $[P_{D1}/P_{D2}]$ dimers.

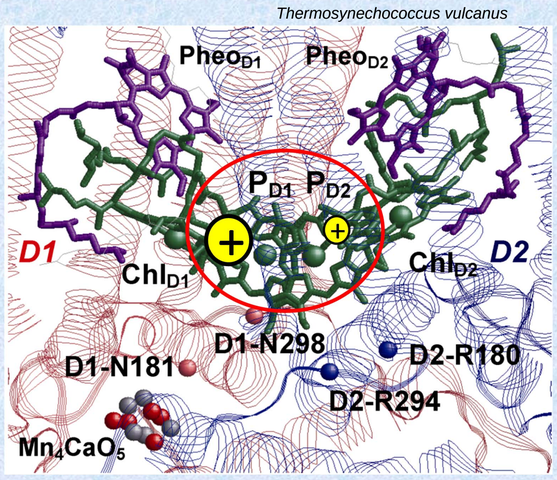
Method

- **QM/MM calculation** of the whole protein-pigment complexes
- **Redox potential calculation** with an electrostatic continuum-model approach

PSII (P_{D1}/P_{D2})

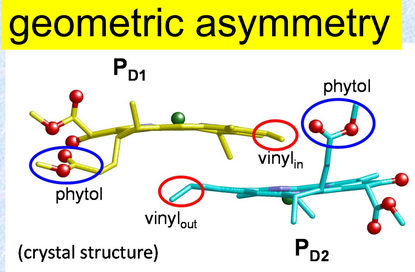
K. Saito, T. Ishida, M. Sugiura, K. Kawakami, Y. Umena, N. Kamiya, J. R. Shen, H. Ishikita, *J. Am. Chem. Soc.* **133** (2011), 14379

Thermosynechococcus vulcanus

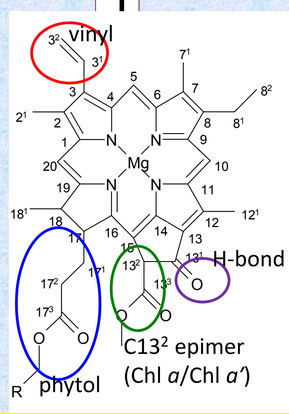


PDB: 3ARC, Umena, Y., Kawakami, K., Shen, J.-R., Kamiya, N. Nature **473:** 55-60 (2011)

geometric asymmetry



(crystal structure)



chlorophyll *a* (chl *a*)

observed $[P_{D1}/P_{D2}]^{\bullet+}$ ratio

$P_{D1}^{\bullet+}:P_{D2}^{\bullet+} = 7:3\text{-}8:2$ in the PSII complex

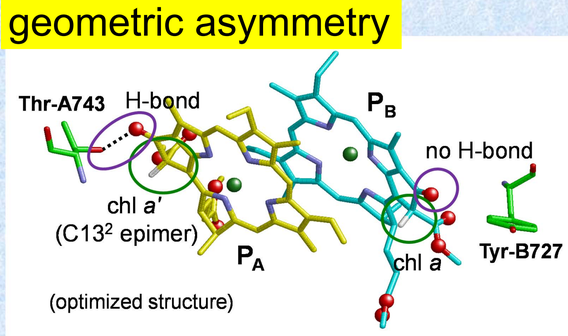
by FTIR, ENDOR and the optical measurement

- **70-80%** of "+" is on P_{D1}.

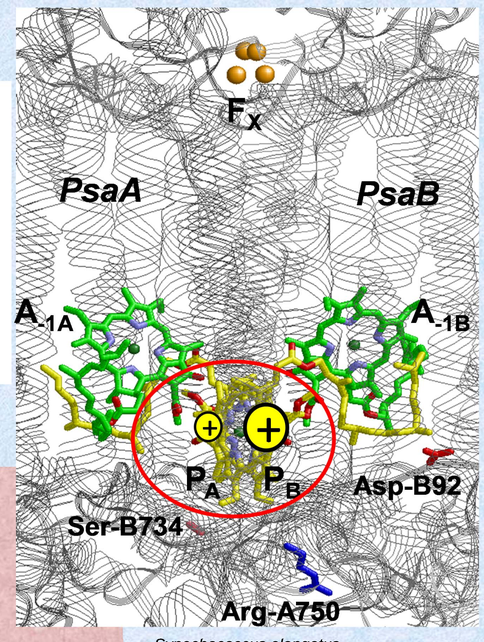
PSI (P_A/P_B)

K. Saito, H. Ishikita, *Biophys. J.* **101** (2011), doi:10.1016/j.bpj.2011.09.010

geometric asymmetry



(optimized structure)



Synechococcus elongatus

PDB: 1JB0, Jordan, P., Fromme, P., Witt, H.T., Klukas, O., Saenger, W., Krauss, N. (2001) Nature **411:** 909-917

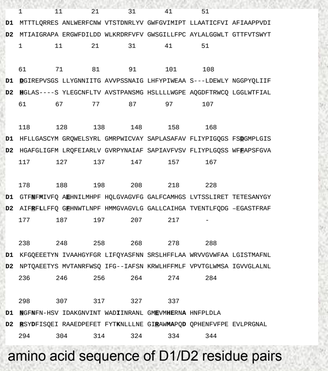
observed $[P_A/P_B]^{\bullet+}$ ratio

$P_A^{\bullet+}:P_B^{\bullet+} =$ **5:5-3:7** by FTIR; **3:7-0:10** by ENDOR, ESSEM and EPR

- **> 50%** of "+" is on P_B.
- In the **H-bond lacking mutant** (T743V and T743A), **more "+"** is on P_A than the wild type.

What does determine the positive charge distribution?

Results of Calculation



amino acid sequence of D1/D2 residue pairs

Positive charge distribution (dimer)

PSII (P_{D1}/P_{D2})

	protein charge		protein spin		vacuum charge		vacuum spin	
	$P_{D1}^{\bullet+}$	$P_{D2}^{\bullet+}$	P_{D1}	P_{D2}	$P_{D1}^{\bullet+}$	$P_{D2}^{\bullet+}$	P_{D1}	P_{D2}
complete PSII ($vinyl_{in}/vinyl_{out}$)	76.9	23.1	80.6	19.4				
D1/D2 PSII ($vinyl_{in}/vinyl_{out}$)	**71.6**	**28.4**	**75.7**	**24.3**	**57.5**	**42.5**	**59.8**	**40.2**
: (a) $\Delta[\Delta E_m$ increasing pairs]	28.7	71.3	28.9	71.1				
: Δ(D1-Asn298/D2-Arg294)	61.7	38.2	65.7	34.3				
: Δ(D1-Asn181/D2-Arg180)	64.4	35.6	67.3	32.7				
: (b) $\Delta[\Delta E_m$ decreasing pairs]	87.9	12.1	93.6	6.4				
: Δ(D1-Ala336/D2-Asp333)	75.1	24.9	80.1	19.9				
: Δ(D1-Met183/D2-Leu182)	74.7	25.3	79.1	20.9				
: Δ[(a) + (b)]	50.2	49.8	53.1	46.9				
(2.1) vinyl group								
P_{D1}-vinyl replaced by the P_{D2}-vinyl geometry ($vinyl_{out}/vinyl_{out}$)	74.6	25.4	78.3	21.7	61.3	38.7	63.3	36.7
phytol deleted P_{D1}/P_{D2}	67.1	32.9	70.6	29.4	53.4	46.6	55.4	44.6
(2.2) phytol group								

(1) residue pair

unrestricted DFT/B3LYP functional, LACVP* (QSite program)

PSI (P_A/P_B)

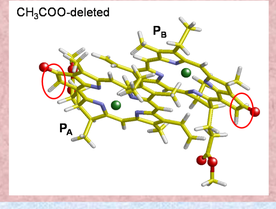
		protein charge		protein spin		vacuum charge		vacuum spin	
		$P_A^{\bullet+}$	$P_B^{\bullet+}$	P_A	P_B	$P_A^{\bullet+}$	$P_B^{\bullet+}$	P_A	P_B
wild type		**27.9**	**72.1**	**22.4**	**77.6**	41.5	58.5	38.1	61.9
(1) H-bond	T743V	32.2	67.8	26.9	73.1	42.8	57.2	39.9	60.1
(2) epimer	CH_3COO- deleted	32.2	67.8	29.7	70.3	45.5	54.5	46.2	53.8
(3) residue pair	Δ(Arg-A750/Ser-B734)	30.6	69.4	25.0	75.0				

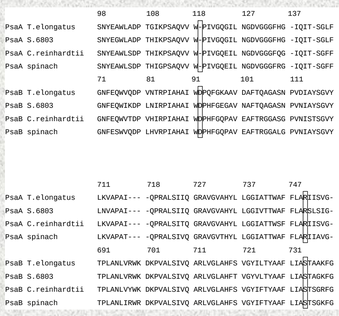
in integrated situations

factors	charge		spin	
	$P_A^{\bullet+}$	$P_B^{\bullet+}$	P_A	P_B
wild type	27.9	72.1	22.4	77.6
(1) + (2)	37.0	63.0	35.1	64.9
(1) + (3)	33.8	66.2	27.6	72.4
(1) + (2) + (3)	40.5	59.5	39.1	60.9

unrestricted DFT/B3LYP functional, LACVP* (QSite program)

CH_3COO-deleted



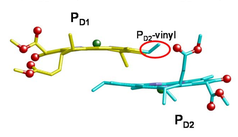


amino acid sequence of PsaA/PsaB residue pairs

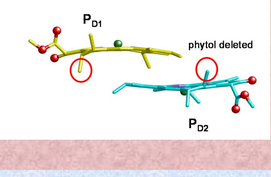
E_m shift vs wild type [mV]

	P_A	P_B
T743V	-9	1

(2.1) P_{D1}-vinyl modeled as P_{D2}-vinyl



(2.2) phytol deleted P_{D1}/P_{D2} models



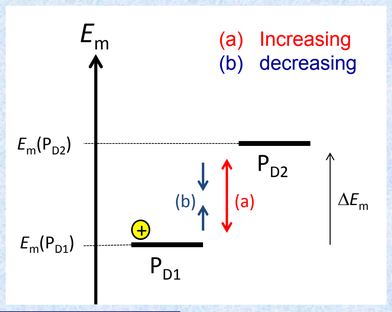
Redox potential E_m (monomer)

PSII

E_m [mV]

	E_m	
	P_{D1}	P_{D2}
PSII	1015-1132	1141-1201

(The fluctuation is due to uncertainty of the protonation state of the Mn_4CaO_5 cluster)



(a) ΔE_m increasing pairs (that contribute to accumulation of $P_{D1}^{\bullet+}$) [> 20 mV]

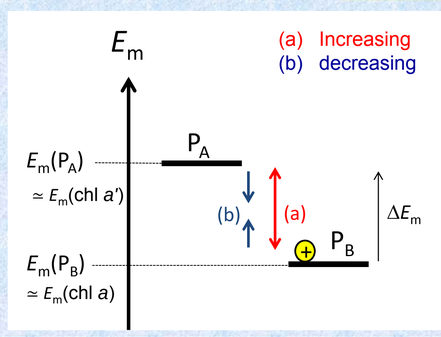
D1 influence			D2 influence			D1/D2 pair influence		
	$E_m(P_{D1})$	$E_m(P_{D2})$		$E_m(P_{D1})$	$E_m(P_{D2})$	$E_m(P_{D1})$	$E_m(P_{D2})$	ΔE_m
D1-Asn181	-8	1	D2-Arg180	69	109	61	110	**49**
D1-Asn298	1	2	D2-Arg294	54	96	55	98	**43**
D1-Asp61	-64	-41	D2-His61	33	50	-31	9	**40**
D1-Glu329	-53	-35	D2-Arg326	49	67	-4	32	**36**
D1-Glu189	-47	-27	D2-Phe188	5	10	-42	-17	**25**
D1-Asp170	-59	-32	D2-Phe169	-4	-9	-63	-41	**22**

(b) ΔE_m decreasing pairs (that contribute to accumulation of $P_{D2}^{\bullet+}$) [> 20 mV]

D1 influence			D2 influence			D1/D2 pair influence		
	$E_m(P_{D1})$	$E_m(P_{D2})$		$E_m(P_{D1})$	$E_m(P_{D2})$	$E_m(P_{D1})$	$E_m(P_{D2})$	ΔE_m
D1-Ala336	2	2	D2-Asp333	-56	-80	-54	-78	**-24**
D1-Met183	13	10	D2-Leu182	18	-1	31	9	**-22**
D1-Asn301	4	2	D2-Asp297	-35	-54	-31	-52	**-21**
D1-Ile320	-2	-1	D2-Lys317	74	52	72	51	**-21**
D1-His332	64	44	D2-Met329	2	2	66	46	**-20**

Linear Poisson-Boltzmann equation (MEAD program)

PSI



(a) ΔE_m increasing pairs (that contribute to accumulation of $P_B^{\bullet+}$) [mV]

PsaA	influence on		PsaB	influence on		influence on
	$E_m(P_A)$	$E_m(P_B)$		$E_m(P_A)$	$E_m(P_B)$	ΔE_m
Arg-A750	65	36	Ser-B734	9	21	17
(absent)			Asp-B92	-15	-24	9

(b) ΔE_m decreasing pairs (that contribute to accumulation of $P_A^{\bullet+}$) [mV]

PsaA	influence on		PsaB	influence on		influence on
	$E_m(P_A)$	$E_m(P_B)$		$E_m(P_A)$	$E_m(P_B)$	ΔE_m
A_{-1A}	-65	-23	A_{-1B}	-19	-41	–28
Gln-A657	-4	-2	Asn-B633	18	26	-14

Linear Poisson-Boltzmann equation (MEAD program)

Conclusion

Origin of the charge distribution

PSII (P_{D1}/P_{D2})

major effect:

- electrostatic asymmetry of the D1/D2 **residue pair**
  ;the ΔE_m increasing pairs

2nd major effect:

- different orientations of P_{D1}/P_{D2} **phytol group**

minor effect:

- different orientations of P_{D1}/P_{D2} **vinyl group**

PSI (P_A/P_B)

major effect:

- **P_A: chl *a*; P_B: chl *a′*** ($C13^2$ **epimer**)
- **H-bond** of Thr A743 with **P_A**; **no H-bond** with **P_B**

minor effect:

- electrostatic asymmetry of the PsaA/PsaB **residue pair**
  ;Arg-A743/Ser-B734

- The calculated values of the positive charge distributions for PSII and PSI were in agreement with the observed values.
- The charge distributions over the dimer were strongly correlated with the redox potential difference of the monomers.
- The **dominant factor** of determining the charge distributions is:
  the **difference** in the **electrostatic protein environments** between **D1** and **D2** for **PSII;**
  the **difference** in the **geometry** between **P_A** and **P_B** (the **H-bond** and the **epimer)** for **PSI.**

Appendix: Observed Positive Charge Distributions

PSII (P_{D1}/P_{D2})

species	mutation	P_{D1}^{+}	P_{D2}^{+}	method	Ref.
spinatch	WT	82	18	ENDOR	5
***Synechocystis* PCC6803**	WT	80	20	optical mesurement	9
Thermosynecococcus elogatus	WT PSII	70-80	30-20	FTIR	10
	WT RC	~50	~50		

PSI (P_A/P_B)

species	mutation	P_A^{+}	P_B^{+}	method	Ref.
***Synechocystis sp.* PCC6803**	WT	50-33	50-67	FTIR	1
***Synechocystis sp.* PCC6803**	WT	0	100	ENDOR/ESSEM	2
spinatch	WT	10	90	ESSEM	3
spinatch	WT	25-20	75-80	ESSEM	4
spinatch	WT	25	75	ENDOR	5
Synechococcus elongatus	WT	<15	>85	EPR/ENDOR	6
Chlamydomonas reinharditii	TV A739	> WT (> 0-50)	< WT (< 50-100)	ENDOR	7
Chlamydomonas reinharditii	TA A739	WT+[14-18] (14-68)	WT-[14-18] (32-86)	FTIR	8
		>WT (> 0-50)	<WT (< 50-100)	ENDOR	

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Salam!
Azərbaycan